

High energy photoionization of fullerenes

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Abstract

We show that the theoretical predictions on high energy behavior of the photoionization cross section of fullerenes depends crucially on the form of the function $V(r)$ which approximates the fullerene field. The shape of the high energy cross section is obtained without solving of the wave equation. The cross section energy dependence is determined by the analytical properties of the function $V(r)$.

1 Introduction

In this paper we calculate the high energy relativistic asymptotics for the photoionization cross section of the valence electrons of fullerenes C_N . We consider the fullerenes which can be treated approximately as having the spherical shape. The photon carries the energy ω and we find the leading term of expansion of the cross section $\sigma(\omega)$ in terms of $1/\omega$. We keep the photon energy to be much smaller than the electron rest energy mc^2 . Here we consider only the ionization of s states.

One usually uses a model central potential $V(r)$ for description of the field created by spherical fullerene with the radius R and the width of the layer $\Delta \ll R$. The general properties of the potential $V(r)$ are well known—see, e.g. [1]. It is located mostly inside the fullerene layer $R - \Delta/2 \leq r \leq R + \Delta/2$ being negligibly small outside. In the simplest (or even the oversimplified [2]) version it is just the well potential which is constant inside the layer and vanishes outside

$$V(r) = -V_0 \theta(r - R + \Delta/2) (1 - \theta(r - R - \Delta/2)); \quad V_0 > 0. \quad (1)$$

One often uses the Dirac bubble potential

$$V(r) = -V_0 \delta(r - R); \quad V_0 > 0. \quad (2)$$

in the fullerene studies [3]. Sometimes model potentials are determined by analytical functions of r with a sharp peak at $r = R$. The Dirac bubble potential can be viewed as the limiting case of Lorentz bubble potential. The latter is determined by the analytical formula

$$V(r) = -\frac{V_0}{\pi} \frac{a}{(r - R)^2 + a^2} \quad (3)$$

The Dirac bubble potential can be treated as the limiting case of this potential at $a \rightarrow 0$. The Gaussian-type potential

$$V(r) = -\frac{V_0}{\pi} \exp \frac{-(r-R)^2}{s^2}, \quad (4)$$

with $s \approx \Delta \ll R$ was employed in [4].

Strictly speaking our analysis is true for the negative ion C_N^- . However, since there are many valence electrons in the fullerene shell, we expect it to be true for photoionization of the neutral fullerene C_N as well. We write the equations for one electron in the initial s state.

As it stands now, the asymptotics for the photoionization cross section is known only for the Dirac bubble potential [5]. It was found to be $\sigma(\omega) \sim (\sin pR)^2/\omega^{5/2}$ with $p = |\mathbf{p}| = (2m\omega)^{1/2}$, while \mathbf{p} is the photoelectron momentum (we employ the system of units with $\hbar = c = 1$). Here we demonstrate that the behavior of the asymptotic cross section is strongly model dependent. It is determined by the analytical properties of the potential $V(r)$. In Sec. 2 we obtain the general equation for the asymptotics of the photoionization cross section. In Sec.3 we calculate the asymptotics for the potentials mentioned in Introduction. We analyze the results in Sec.4.

2 Asymptotics of the cross section

We write the following equations for one electron in the ionized s state. The photoionization cross section can be presented as

$$d\sigma = \frac{mp}{(2\pi)^2} |F|^2 d\Omega, \quad (5)$$

with Ω the solid angle of the photoelectron, while F is the photoionization amplitude. Averaging over polarizations of the incoming photon is assumed to be carried out.

In the asymptotics the photon energy ω is much larger than the ionization potential I of the electron bound in the fullerene shell. Limiting ourselves by the condition $\omega \ll m$ we can treat the photoelectron in nonrelativistic approximation. The kinetic energy of the photoelectron is $\varepsilon = \omega - I = p^2/2m$. In the asymptotics $\omega \gg I$ and the electron momentum p strongly exceeds the characteristic momentum μ of the bound state ($p \gg \mu$), and at $\omega \gg I$ the photoionization requires large momentum $\mathbf{q} = \mathbf{k} - \mathbf{p}$ to be transferred to the recoil fullerene. Here \mathbf{k} the photon momentum. One can see that $k = |\mathbf{k}| \ll p$ if $I \ll \omega \ll m$ and thus we can put $q = p$.

If the electron-photon interactions are written in the velocity form, momentum \mathbf{q} is transferred in the initial state [6], [3] in ionization of s states. Thus the photoelectron can be described by plane wave. The amplitude of photoionization can be written as

$$F = N(\omega) \frac{\mathbf{e} \cdot \mathbf{p}}{m} \psi(p); \quad N(\omega) = \left(\frac{4\pi\alpha}{2\omega} \right)^{1/2}. \quad (6)$$

We replaced q by p in the argument of the Fourier transform of the wave function of the fullerene electron $\psi(r)$. The latter is $\psi(p) = \int d^3r \psi(r) e^{-i\mathbf{p}\mathbf{r}}$. We employed that the s state wave function does not depend on the direction of the vector \mathbf{r} .

Now we present the wave function $\psi(p)$ in terms of the Fourier transform of the potential

$$V(p) = \int d^3r V(r) e^{-i\mathbf{p}\mathbf{r}} = \frac{4\pi}{p} \int_0^\infty dr r V(r) \sin pr. \quad (7)$$

The function $\psi(p)$ at $p \gg \mu$ can be expressed by the Lippmann–Schwinger equation [3]

$$\psi = \psi_0 + G(\varepsilon_B)V\psi, \quad (8)$$

with G the electron propagator of free motion, $\varepsilon_B = -I$. The matrix element of the propagator is

$$\langle \mathbf{f}_1 | G(\varepsilon_B) | \mathbf{f}_2 \rangle = g(\varepsilon_B, f_1) \delta(\mathbf{f}_1 - \mathbf{f}_2); \quad g(\varepsilon_B, f_1) = \frac{1}{\varepsilon_B - f_1^2/2m}.$$

For a bound state $\psi_0 = 0$, and thus Eq.(8) can be evaluated as $\psi(p) = \langle \mathbf{p} | GV | \psi \rangle = g(\varepsilon_B, p)J(p)$ with

$$J(p) = \int \frac{d^3 f}{(2\pi)^3} \langle \mathbf{p} | V | \mathbf{f} \rangle \langle \mathbf{f} | \psi \rangle.$$

The integral $J(p)$ is saturated at $f \sim \mu \ll p$. Thus we can put $\langle \mathbf{p} | V | \mathbf{f} \rangle = \langle \mathbf{p} | V | 0 \rangle = V(p)$. Putting also $g(\varepsilon_B, p) = -2m/p^2$ we obtain [3]

$$\psi(p) = -\frac{2m}{p^2}V(p)\psi(r=0) = -\frac{1}{\omega}V(p)\psi(r=0). \quad (9)$$

Thus Eq.(6) can be written as

$$F = -2N(\omega) \frac{\mathbf{e} \cdot \mathbf{p}}{p^2} V(p) \psi(r=0), \quad (10)$$

and the asymptotics of the photoionization cross section can be expressed through the potential $V(p)$:

$$\sigma(\omega) = \frac{4\alpha}{3} \frac{p}{\omega^2} |V(p)|^2 \psi^2(r=0); \quad p = \sqrt{2m\omega}. \quad (11)$$

Recall that this equation is written for the case when there is one electron in the s state. Thus one can find the asymptotic energy dependence of the photoionization cross section without solving the wave equation.

3 Asymptotics for the model potentials

Start with the Dirac bubble potential given by Eq.(2). We find immediately

$$V(p) = -V_0 \frac{4\pi R}{p} \sin pR. \quad (12)$$

Employing Eq.(11) we find for the asymptotic cross section

$$\sigma = \frac{2^8 \alpha \pi^2 V_0^2 m^2 R^2}{3 p^5} \sin^2(pR) \psi^2(0); \quad p^2 = 2m\omega. \quad (13)$$

This is just the result obtained in [5] by solving the wave equation.

It is instructive to compare the result with that for the well potential determined by Eq.(1). Direct calculation provides

$$V(p) = \frac{4\pi V_0}{p^3} (f(R_2) - f(R_1)),$$

with $f(R) = pR \cos pR - \sin pR$ and $R_{2,1} = R \pm \Delta/2$. In the asymptotics

$$V(p) = \frac{4\pi V_0 R}{p^2} (\cos pR_1 - \cos pR_2) \quad (14)$$

Here we neglected the terms of the order Δ/R . The width Δ is of the order of one atomic unit. Thus it is reasonable to assume that $p \gg 1/\Delta$ at $\omega \gg I$. The asymptotic cross section is thus

$$\sigma = \frac{2^9 \alpha \pi^2 V_0^2 R^2 m}{3 \omega p^5} \sin^2(pR) \sin^2(p\Delta/2) \psi^2(0); \quad p^2 = 2m\omega. \quad (15)$$

Both Dirac bubble and well potentials have singularities on the real axis. However, the wave functions exhibit different behavior at the singular points. This leads to different high energy behavior in these cases. The wave function corresponding to the Dirac bubble potential is continuous at $r = R$ while its first derivative suffers a jump at this point [5]. Thus presenting

$$\psi(p) = \frac{4\pi}{p} \left[\int_0^{R^-} dr \sin pr \psi(r) r + \int_{R^+}^{\infty} dr \sin pr \psi(r) r \right]; \quad R^\pm = R \pm \delta; \quad \delta \rightarrow 0. \quad (16)$$

we find after two integrations by parts

$$\begin{aligned} \psi(p) &= \frac{4\pi}{p^3} R \sin(pR) [\psi'(R^-) - \psi'(R^+)] \\ &\quad - \frac{4\pi}{p^3} \left[\int_0^{R^-} dr \sin pr (\psi''(r)r + 2\psi'(r)) + \int_{R^+}^{\infty} dr \sin pr (\psi''(r)r + 2\psi'(r)) \right] \end{aligned} \quad (17)$$

Further integration by parts of the second term demonstrates that it is about $1/p$ times the first one. Hence the leading contribution is provided by the first term and the Fourier transform of the function $\psi(r)$ is determined by the jump of the first derivative. This leads to the $\omega^{-5/2}$ law for the cross section—see Eqs.(11,12). In the case of the well potential one can present the function $\psi(p)$ in the form similar to Eq.(16) but with two singular points $r = R_{2,1} = R \pm \Delta/2$. The first derivatives $\psi'(r)$ are continuous at these points while the second derivatives suffer jumps. [7]. After three integrations by parts we find

$$\psi(p) = \frac{4\pi}{p^4} f(R, \Delta),$$

with $f(R, \Delta) = -2\psi'(0) + R_1\beta(R_1) \cos pR_1 + R_2\beta(R_2) \cos pR_2$, where $\beta(R_{1,2})$ are the jumps of the second derivative ψ'' . The wave equation at $0 \leq r \leq R_1$, which is $\psi''(r) + 2\psi'(r)/r = -2m\varepsilon_B \psi(r)$ requires that $\psi'(0) = 0$. Thus in the lowest order of expansion in Δ/R we find

$$\psi(p) = \frac{4\pi}{p^4} R \left(\cos(pR_1) \beta(R_1) + \cos(pR_2) \beta(R_2) \right). \quad (18)$$

Thus the asymptotic wave function in the field of the well potential is $1/p$ times that in Dirac bubble potential. This provides additional small factor of the order $1/\omega$ in the photoionization cross section given by Eq.(15).

Turn now to the Lorentz bubble potential determined by Eq.(3) assuming that $a \ll R$. Employing Eq.(7) and changing the variable of integration $x = r - R$ we present the Fourier transform of the potential as

$$V(p) = -4\frac{aV_0}{p}(V_1(p) + V_2(p)); \quad V_1(p) = R \int_{-R}^{\infty} dx \frac{\sin p(R+x)}{x^2 + a^2}; \quad (19)$$

$$V_2(p) = \int_{-R}^{\infty} dx x \frac{\sin p(R+x)}{x^2 + a^2}.$$

We present also $V_1 = V_{1a} + V_{1b}$ with

$$V_{1a} = R \sin pR \int_{-R}^{\infty} dx \frac{\cos px}{x^2 + a^2}; \quad V_{1b} = R \cos pR \int_{-R}^{\infty} dx \frac{\sin px}{x^2 + a^2}.$$

One can write

$$V_{1b} = R \cos pR \int_R^{\infty} dx \frac{\sin px}{x^2 + a^2},$$

since the integrand is the odd function of x , and the integral in the interval $-R \leq x \leq R$ turns to zero. The condition $a \ll R$, enables us to neglect V_{1b} and to replace the lower limit of integration in V_{1a} by $-\infty$. Thus

$$V_1(p) = V_{1a}(p) = R \sin pR \int_{-\infty}^{\infty} dx \frac{\cos px}{x^2 + a^2} = \pi \frac{R}{a} e^{-pa} \sin pR. \quad (20)$$

In similar way we obtain

$$V_2(p) = \pi e^{-pa} \cos pR. \quad (21)$$

Hence $|V_2(p)| \ll |V_1(p)|$, and

$$V(p) = -4\frac{aV_0}{p}V_1(p) = -4\pi \frac{RV_0}{p} e^{-pa} \sin pR. \quad (22)$$

The photoionization cross section is thus

$$\sigma = \frac{2^8}{3} \frac{\alpha \pi^2 V_0^2 m^2 R^2}{p^5} e^{-2pa} \sin^2(pR) \psi^2(0); \quad p^2 = 2m\omega. \quad (23)$$

It differs from the cross section for the Dirac bubble potential by the exponential factor e^{-2pa} . Note that the exponential drop can be viewed as due to the singularities of the function $V(r)$ in the complex plane. It has poles at $r = R \pm ia$.

In similar way we find for the Gaussian type potential given by Eq.(4)

$$V(p) = -\frac{4\pi^{1/2}}{p} R s V_0 e^{-p^2 s^2/4} \sin pR, \quad (24)$$

which has essential singularity at infinity. Thus in this case the cross section behavior exhibits Gaussian drop

$$\sigma = \frac{64\alpha\pi}{3} \frac{R^2 s^2 V_0^2}{\omega^2 p} e^{-p^2 s^2/2} \sin^2(pR) \psi^2(0). \quad (25)$$

4 Summary

We found that the high energy behavior of the photoionization cross section of fullerenes depends on the form of function $V(r)$ which is chosen for approximation of the fullerene field. We expressed the asymptotic cross section in terms of the Fourier transform $V(p)$ of the potential $V(r)$. The shape of the function $V(p)$ at large p is known to be determined by the analytical properties of the function $V(r)$ [8]. Thus the latter determine the shape of the asymptotic cross section as well.

The well potential and the Dirac bubble potential presented by Eqs.(1) and (2) with singularities on the real axis lead to the power drop of the cross section. The Lorentz bubble potential given by Eq.(3) having poles at finite values of r in the complex plane provide the exponential drop of the cross section. Finally the Gaussian type potential determined by Eq.(4) with the essential singularity at infinity provides the Gaussian drop of the cross section.

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